ELSEVIER

Catalysis Today 75 (2002) 49–55

CATALYSIS TODAY

www.elsevier.com/locate/cattod

New insight in the solid state characteristics, in the possible intermediates and on the reactivity of Pd–Cu and Pd–Sn catalysts, used in denitratation of drinking water

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Abstract

Bimetallic palladium-based supported catalysts were tested in the liquid phase hydrogenation of nitrates. They were characterised by XPS, CO chemisorption, TPD–TPR and DRIFT. The effect of the preparation method, the support, the precursors, the relative amount of active metals and their role in the formation of intermediates and products are tentatively discussed. The catalytic activity and the formation of intermediate nitrite depend on the Pd–Cu ratio. Catalysts presenting a Pd/Cu atomic ratio >1 display the highest activity and the lowest intermediate nitrite than those presenting a Pd/Cu atomic ratio <1. Sol–gel method gives catalysts with a high activity and a low nitrite formation. The Pd–Cu-based catalyst supported on zirconia is more active and selective in N_2 compared to the corresponding Pd–Sn catalyst. An enrichment of the surface by Pd is responsible for a low intermediate nitrite formation and high selectivity in N_2. The reduction of NO is activated on Pd–Cu catalysts, contrary to Pd–Sn catalysts. Sn promotes the formation of ammonia.

Keywords: Catalyst; Nitrate; Surface characterisation; Palladium; Alumina; Zirconia

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1. Introduction

Intensive nitrogen fertilisation, agricultural activities and NO_x emissions from combustion processes lead to pollution of groundwater that exceeds the tolerated levels in the European Union (EC directive 80/778: maximum nitrate concentration 50 mg/dm^3).

Various established processes are available for nitrate removal from water. Ion exchange, reverse osmosis or microbiological treatments between others. However, in most cases, these techniques require a post-treatment of effluents and cannot be easily adapted to variable nitrate contents or water flow. In the last decade, catalytic hydrogenation of nitrate has been proposed to address this problem [1–15]. Main advantages of this technique are a lower waste generation and a higher space–time-yield but its main drawback is associated with the formation of ammonia as a result of over oxidation, and of nitrite as intermediate. Both of them face a strict admissible level of 0.1 and 0.5 mg/dm^3, respectively. With reference to industrial applications, porous ceramic membranes modified by insertion of active metals have been developed [10,12].

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PII: S0920-5861(02)00043-3

Fundamental studies, which could allow the understanding of the formation of nitrite, ammonia and nitrogen are scarce [4,5,14,15]. The aim of this paper is to give some additional light on these aspects. Catalyst powders containing Pd–Sn or Pd–Cu bimetallic catalysts deposited on alumina or zirconia were prepared and tested in the decomposition of water containing nitrates. XPS, CO chemisorption, TPD–TPR and DRIFT (quasi in situ) techniques were used in order to determine the solid state characteristics, the possible intermediates and their reactivity.

2. Experimental

2.1. Co-precipitation (CP)

Nitrate salts of alumina and copper were co-precipitated by the addition of ammonia at pH $= 7$. The precipitate was filtered, washed, dried and calcined for 3 h at 400 °C in air. Textural parameters were BET surface area $= 260\,m^2/g$, D_{pores} av. $= 1.6$ nm, $V_p = 0.19\,cm^3/g$. It was impregnated with $PdCl_2$ in acetone. The powder was dried and sieved to obtain a grain size of 20–50 μm. The samples were finally calcined in air at 280 °C/2 h, followed by a reduction in hydrogen at 150 °C/1 h. These catalysts will be mentioned as CPAlCu(x)Pd(y), with x and y expressed in weight percentages of Cu and Pd.

2.2. Sol–gel (SG)

A solution of water dispersible alumina and copper acetate was added in the presence of polyvinylalcohol and isooctyl-phenoxyethanol and dropped into a bath containing tetramethyl-ammonium hydroxide. The gel spheres were aged for 1 h. Gel beads were washed down to pH $= 10$, dried by azeotropic dehydration in toluene and calcined in air at 550 °C/3 h. Samples were impregnated with $PdCl_2$ in HCl. The powder was dried and further reduced in H_2 at 160 °C. The beads were crushed to obtain a grain size of 20–50 μm. Samples were calcined in air at 500 °C/2 h and then reduced in hydrogen at 350 °C/1 h. These catalysts will be mentioned as SGAlCu(x)Pd(y), with x and y expressed as above. Textural parameters were BET surface area $= 314\,m^2/g$, D_{pores} av. $= 4.6$ nm, $V_p = 0.61\,cm^3/g$ for the SGCu(5)Pd(2), BET surface area $= 375\,m^2/g$, D_{pores} av. $= 4.7$ nm, $V_p = 0.89\,cm^3/g$ for the SGCu(2)Pd(5).

2.3. Impregnation of SG microspheres (MS)

Zirconia microspheres (32–50 μm) were prepared by gel-supported precipitation [16], azeotropically dried and calcined in air at 550 °C for 3 h. Textural parameters were BET surface area $= 112\,m^2/g$, D_{pores} av. $= 8.2$ nm, $V_p = 0.25\,cm^3/g$. Powder catalysts were prepared by impregnation methods starting from aqueous solutions of $PdCl_2$, $Pd(OAc)_2$, $CuCl_2$, $Cu(OAc)_2$, $SnCl_2$. They were calcined in air at 500 °C for 1 h and reduced in hydrogen flow at 130 °C (150 °C in the case of Sn-containing catalyst) for 1 h. These catalysts will be mentioned as follows: MSZrCu(or Sn)(x)Pd(y), with x and y expressed in weight percentages of Cu (or Sn) and Pd. (Cl) and (OAc) indicate chloride or acetate salts, respectively.

2.4. Catalytic tests

2.4.1. SG and CP catalysts

Catalysts were tested in a thermostated (10 °C) batch reactor (700 cm^3) equipped with a pH-stat, H_2 inlet and outlet and a sampling port. The catalyst (700 mg) was suspended in pure water and saturated with hydrogen for 90 min under vigorous stirring. The pH of the solution was set at 6 and maintained constant through the reaction. A solution containing nitrate was introduced and the time was started. The nitrate concentration was equal to100 ppm.

2.4.2. MS-zirconia supported catalysts [12]

Catalysts (40 mg in 63 cm^3 of pure water) were tested at 25 °C and saturated with hydrogen for 1 h. The pH of the solution was set at 5. Samples were periodically taken from the suspension and analysis of nitrate and nitrite concentrations was performed by ion chromatography. Ammonia concentration was determined with the use of a gas sensitive electrode.

2.5. Characterisation methods

2.5.1. TPD–TPR

The adsorption of NO was realised at room temperature. It was followed by a TPD to 150 °C (2 °C/min) under helium flow (50 cm^3/min). The catalyst was then cooled down at room temperature and a new adsorption of NO was carried out. A TPR in the presence of hydrogen was then performed from room temperature to temperatures higher than 300 °C. The same protocol was applied after adsorption of 1 cm^3 of a solution of nitrate or nitrite salt on the catalyst.

2.5.2. DRIFT

DRIFT spectra were recorded by a IFS 88 Bruker Fourier transform spectrophotometer with a pretreatment in situ cell. The spectra were recorded in absorbency mode. Spectra were obtained after adsorption of nitrates (1 cm^3 of a solution of nitrate or nitrite salt 10^{-2} M). They were recorded at 250 °C, under a flow of H_2/He (20 cm^3/min).

2.5.3. XPS

XPS analysis was performed with an SSX-10 model 206 X-ray photoelectron spectrometer from fisons. The analysis chamber was operated under ultrahigh vacuum with a pressure close to 5.10^{-9} Torr. X-rays were produced by a monochromatized aluminium anode (Al Kα = 1486.6 eV). The surface positive charge was compensated by a floodgun. The binding energy (BE) values were referred to the C1s peak at 284.8 eV. Atomic concentration ratios were calculated by correcting the intensity ratios with the theoretical sensitivity factors based on Scofield cross-sections. The following lines were used for the quantitative analysis: Pd3d, Cu2p, Al2p, Sn3d and Zr3d. As the mean free path of the photoelectrons is typically between 2 and 6 nm, the information obtained from this technique corresponds to the uppermost atomic layers of the surface (about 10–20) of the catalyst. The experimental error of XPS measurement for BE could be considered to about 0.2 eV.

2.5.4. CO chemisorption analysis

CO chemisorption analysis was carried out on a Micromeritics PulseChemiSorb 2705 system. Sample was pretreated with He and after with H_2 at 150 °C for 1 h, then was heated at 250 °C under a stream of helium during 2 h. The temperature was finally decreased to room temperature and pulses of CO were introduced. The amount of CO adsorbed was measured and the dispersion of Pd was calculated assuming that one Pt atom chemisorbs one atom of CO using the following formula, Pt dispersion = number of CO molecules chemisorbed by Pt/ number of total Pt atoms in the catalyst.

3. Results

3.1. CP and SG catalysts

Catalytic activities are presented in Table 1. SG catalysts are more active than CP catalysts. The SGAlCu(2)Pd(5) catalyst displays a better activity and a lower intermediate nitrite formation than the SGAlCu(5)Pd(2) one. All catalysts present a similar selectivity in ammonia.

The bulk Pd/Cu atomic ratio of the CPAlCu(5)Pd(2) catalyst is about the same as the XPS Pd/Cu atomic ratio (Table 2). This indicates that Pd and Cu are nearly homogeneously distributed on the particles.

The Pd/Cu bulk atomic ratio of the SGAlCu(5)Pd(2) catalyst, is lower by a factor of 1.5 than the XPS Pd/Cu atomic ratio. Surface appears to be enriched in Pd. The SGAlCu(2)Pd(5) catalyst presents a bulk Pd/Cu atomic ratio higher than the XPS Pd/Cu atomic ratio. The XPS Pd/support atomic ratio is higher in SG catalysts compared with the CP catalyst, indicating that in SG catalysts, the surface is more enriched in Pd.

After the reaction, SG catalysts present a slight change of the XPS Pd/Cu atomic ratio. Contrary to SG catalysts, the Pd/Cu ratio of the CP catalyst varies dramatically. Simultaneously, the XPS Pd/support atomic ratio increases after the test by a factor of 1.8 and the XPS Cu/support atomic ratio decreases by

Table 1
Catalytic performances of CP and SG catalysts

Catalyst	Nitrate removal activity (mg nitrate/h $g_{catalyst}$)	Maximum nitrite (mg/l × 100 ppm nitrate removal)	Ammonium (mg/l × 100 ppm nitrate removal)
CPAlCu(5)Pd(2)	5	35	13
SGAlCu(5)Pd(2)	32	34	18
SGAlCu(2)Pd(5)	47	2	17

Table 2
XPS surface composition of SG and CP catalysts (atomic percentages) and Pd dispersion values (CO chemisorption)[a]

Catalyst	XPS Pd/support before/after the catalytic test	XPS Cu/support before/after the catalytic test	XPS Pd/Cu before/after the catalytic test	Pd/Cu bulk	Pd dispersion (%)
SGAlCu(2)Pd(5)	0.014/0.011	0.012/0.011	1.17/1.0	1.61	3
SGAlCu(5)Pd(2)	0.009/0.008	0.016/0.020	0.56/0.4	0.35	2
CPAlCu(5)Pd(2)	0.006/0.011	0.020/0.008	0.30/1.5	0.31	13

[a] Pd/Cu bulk: Pd and Cu contents were determined by atomic absorption analysis.

a factor of 2.5. This behaviour could be ascribed either to a segregation of Pd on the surface, or to a migration of copper inside the pores or both.

CO chemisorption on a monometallic CPAlCu(5) catalyst indicates that CO is not chemisorbed on Cu. SG catalysts display lower Pd dispersion values compared to the CP one (Table 1).

3.2. Zirconia microspheres supported catalysts

3.2.1. Effect of the precursor

The use of metal acetate precursors (MSZr(OAc) Cu(1.5)Pd(5)) allows to obtain the same activity as chloride precursors (MSZr(Cl)Cu(1.5)Pd(5)). However, the formation of both ammonia and nitrite is enhanced on the catalysts prepared with acetate precursors (Table 3). Besides, the XPS Pd/Cu atomic ratio was found to be near 1.13 for chloride catalysts and near 0.33 for the acetate catalysts. The XPS Pd/support atomic ratio of the catalyst prepared using acetate precursors is much lower (0.02) than the one obtained for the catalyst prepared using the chloride precursor (0.07) (Table 4). This result is in line with CO chemisorption measurements. Indeed, it was found that the catalyst prepared with chloride precursors display the highest Pd dispersion values, namely 19% against 8% for the catalyst prepared using acetate precursors. Besides, the XPS Cu/support atomic ratio of the catalyst prepared using acetate precursors is similar to the one found with catalysts prepared with chloride precursors.

3.2.2. Effect of the promoter

The presence of Sn induces a dramatic decrease in the activity and selectivity in N_2, compared to the catalyst modified by Cu (Table 3). No intermediate nitrite is formed on this catalyst.

3.2.3. TPD–TPR experiments

TPD performed on the MSZr(Cl)Cu(1.5)Pd(5) catalyst show that NO is not decomposed from room temperature to 150 °C. The TPR profile of NO under H_2 presents a peak between 40 and 80 °C, at $m/e = 44$, which shows that NO is reduced into N_2O. Nitrates are

Table 3
Catalytic performances of the Pd–promoter/ZrO_2 catalysts

Catalyst	Initial rate (ppm/min)	Maximum nitrite (ppm)	Ammonia (ppm)	N_2 selectivity (%)
MSZr(OAc)Cu(1.5)Pd(5)	9.20	41	19	30
MSZr(Cl)Cu(1.5)Pd(5)	9.10	15	12	54
MSZr(Cl)Sn(1.5)Pd(5)	0.25	0	24	12

Table 4
XPS surface composition of MSZr-supported catalysts (atomic percentages) and Pd dispersion values (CO chemisorption)

Catalysts	XPS Pd/support	XPS Cu/support	XPS Pd/Cu	Pd dispersion (%)
MSZr(Cl)Cu(1.5)Pd(5)	0.07	0.06	1.13	19
MSZr(OAc)Cu(1.5)Pd(5)	0.02	0.06	0.33	8

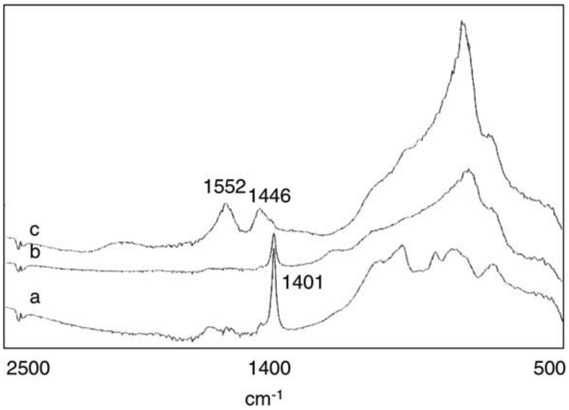

Fig. 1. Drift analysis: (a) MS(Cl)ZrSn(2)Pd(5), (b) MS(Cl)ZrCu (1.5)Pd(5) and (c) MS(Cl)ZrSn(2)Pd(5) after reaction.

not reduced in the temperature range studied. Ammonia was never observed. On the MS(Cl)ZrSn(2)Pd(5) catalyst, the TPR profile shows that this catalyst is not reactive towards the reduction of NO.

3.2.4. DRIFT experiments

Spectra of the MS(Cl)ZrSn(2)Pd(5) catalyst, after adsorption of nitrates, were recorded between 500 and 4400 cm^{-1}, before and after the reduction of adsorbed species under H_2. In both cases, a main peak at about 1401 cm^{-1} corresponding to NH species is observed (Fig. 1). This catalyst, after reaction, shows important peaks at 1446 and 1552 cm^{-1} which could be attributed to ammonia remains on the catalyst, after the reaction. It is noteworthy that Sn promotes the formation of ammonia. The spectrum recorded after reduction of adsorbed nitrite on MC(Cl)ZrSn(2)Pd(5) showed that the formation of NH species (1401 cm^{-1}) is smaller than the one observed after the adsorption of nitrates. This could be an indication that ammonia is probably formed by the reduction of nitrates in this catalysts. In the MS(Cl)ZrCu(1.5)Pd(5) catalyst, the peak at 1401 cm^{-1} is significantly lower.

4. Discussion

4.1. Effect of the preparation procedure: CP and SG catalysts

XPS analysis before and after the catalytic test has shown that the XPS Pd/Cu atomic ratio of SG catalysts remains nearly unchanged. On the contrary, the XPS Pd/Cu, Cu/support and Pd/support atomic ratios of the CP catalyst change dramatically during the catalytic test. This lack of stability could explain the low activity of CP catalyst, compared to the SG ones. A loss of concentration of Cu on the surface could explain these results. An agglomeration of Cu occurs probably on the surface during the reaction. Another possible assumption is the leaching of metals in the solution or a migration of Cu inside the pores of the support. The preparation procedure and the amount of Cu do not influence significantly the concentration of Cu on the surface. When the Pd content is too high, either some agglomeration of the Pd occurs on the surface, or Pd is also deposited in the more internal surface of the pores of the catalyst support.

4.2. Effect of the relative amount of active metals on the activity and in the formation of nitrite and ammonia

The Pd–promoter ratio is known to affect considerably the activity and the selectivity of the catalyst in the hydrogenation of nitrate [3]. The SGAlCu(2)Pd(5) catalyst displays a XPS Pd/Cu atomic ratio equal to 1.17 (bulk Pd/Cu is 1.61) and presents the highest activity but also the lowest formation of intermediate nitrite. The low formation of nitrite on the SGAlCu(2)Pd(5) catalyst does not allow to obtain a decrease in the formation of ammonia. The SGAlCu(5)Pd(2) catalyst displays a XPS Pd/Cu atomic ratio equal to 0.56 (bulk Pd/Cu is 0.35). This catalyst is less active than the previous one and leads to a higher intermediate nitrite formation. This indicates that the reduction of nitrite is probably in relation with a higher concentration of Pd on the surface. However, the presence of more Pd on the surface of the SGCu(2)Pd(5) catalyst (or eventually a better interdispersion between Pd and Cu) cannot allow to decrease the formation of ammonia. The fact that for the catalysts containing a higher amount of Pd (namely the SGAlCu(2)Pd(5) catalyst) the XPS Pd/Cu atomic ratio is lower that the bulk Pd/Cu atomic ratio, indicates that when the amount of Pd is too high, an agglomeration of Pd on the surface occurs. It is not excluded that some Cu is deposited over Pd particles but we have not arguments to support that. When the Cu content increases, the XPS Pd/Cu atomic ratio is near the bulk value and the Cu/support atomic ratio remains nearly unchanged. In all cases, the amount of ammonia is the same. On the other hand, Sn promotes the formation of ammonia, which is probably formed by the reduction of nitrates.

4.3. *Influence of the dispersion palladium on the selectivity in N_2*

The MSZr(Cl)Cu(1.5)Pd(5) catalyst prepared with chloride precursors displays a good activity. Pd dispersion is 19% and the XPS Pd/Cu atomic ratio is equal to 1.13 (Table 4). In the catalyst prepared with acetate precursors, the XPS Pd/support atomic ratio (0.02) and the Pd dispersion (8%) are lower compared to the catalyst prepared by chloride precursors. In the MSZr(Cl)Cu(1.5)Pd(5) catalyst, surface enriched in Pd favours the reduction of nitrite into nitrogen The catalyst prepared with acetate precursors displays a higher intermediate nitrite formation and a lower selectivity in N_2. Acetate is probably not entirely removed from the surface and remains on Pd, then the concentration of Pd on the surface is lower and consequently, the reduction of nitrite to N_2 is inhibited. In both cases, the ammonia formation is high.

The activity and the formation of intermediate nitrite seem to depend on the Pd–Cu ratio. The selectivity in N_2 depends on the presence and dispersion of Pd. Sn promotes the formation of ammonia and the low selectivity in N_2.

4.4. *Determination of the possible intermediates and of their relative reactivity*

It was showed that Cu, contrary to Sn, promotes the reduction of NO into N_2O on the MSZr(Cl) Pd(5)Cu(1.5) catalyst. N_2O is assumed to be an intermediate in the hydrogenation of nitrates and the precursor of N_2 formation in the nitrates hydrogenation process [10]. In the same way, during the reduction of nitrates, the MSZrCu(1.5)Pd(5) catalyst leads to a lower amount of ammonia than the MSZr(Cl)Sn(2)Pd(5) catalyst (DRIFT). Besides, catalytic test results showed that the Sn-promoted catalyst is less active but also less selective in nitrogen than the corresponding Cu-promoted catalyst. The selectivity of the reaction could be explained considering that nitrates would lead to NO and N_2O as intermediates on the Cu-promoted catalyst. Then N_2O would lead easily to N_2 (TPR). On the Sn-promoted catalyst, the activation of NO would be more difficult and the hydrogenation process would not favour N_2O formation and consequently, the N_2 formation is inhibited.

It has been reported in the literature that contrary to Cu, Sn enhances the adsorption of hydrogen on Pt [17]. The competition of adsorption between hydrogen and adsorbed nitrite species, would be modified in favour of hydrogen, leading to an increase in the selectivity in ammonia. TPR experiments have shown that NO is not reduced into N_2O, on Pd–Sn catalysts. This can be due to a lack of reactivity of NO, on Pd–Sn catalysts. However, if we assume that the competition of adsorption between hydrogen and nitrite is in favour of hydrogen, the recombination of NO adsorbed species into N_2O adsorbed species, would be more difficult. This could explain why N_2O is not observed as intermediate on Pd–Sn catalysts (TPR). In the literature [8], Pd–Sn catalysts are reported to be better catalysts than Pd–Cu catalysts, but these results were obtained on catalysts supported on alumina. The formation of a spinel-type-copper-aluminate phase, in contrast to zirconia, was proposed to explain these results [12,18]. The poor catalytic activity of Pd–Sn catalysts, could also be explained, assuming that the Pd–Sn ratio used for the catalytic tests was not optimised [15].

5. Conclusions

XPS measurements have shown that the Pd–Cu catalysts prepared by CP are not stable during the catalytic test, contrary to catalysts prepared by the SG technique. Whatever the preparation technique used (CP, SG, impregnation of zirconia microspheres), the catalytic activity and the formation of intermediate nitrite depends on the Pd–Cu ratio. Highest activities and lowest intermediate nitrite are found for Pd/Cu bulk atomic ratios higher than 1 (catalysts prepared with chloride precursors). Moreover, free Pd atoms favour the reduction of nitrite into N_2. The Pd–Cu-based catalyst supported on zirconia is more active and selective in N_2 compared to the corresponding Pd–Sn catalyst. The reduction of NO is activated by Cu. On the contrary, under the conditions used in this work, Sn promotes the formation of ammonia and the low selectivity in N_2.

Acknowledgements

The European Community is gratefully acknowledged for financial support: contract BRPR-CT97-3527. Dr. Seong Moon Young is acknowledged for his help in the use of TPD–TPR analysis. The authors thank the Fonds National de la Recherche Scientifique (Belgium), for financing the laboratory equipment used in this research.

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